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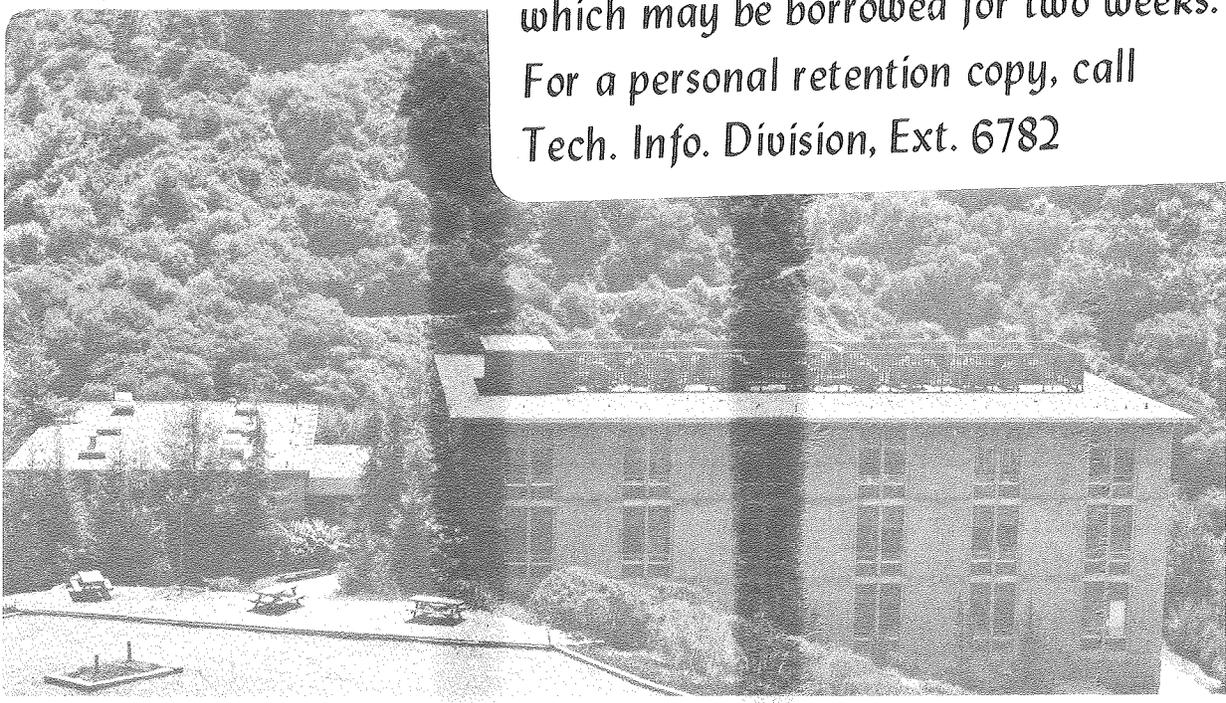
EFFECTS OF LEWIS ACID CATALYSTS ON THE HYDROGENATION
AND CRACKING OF TWO-RING AROMATIC AND HYDROAROMATIC
STRUCTURES RELATED TO COAL

Sadie S. Salim and Alexis T. Bell

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Effects of Lewis Acid Catalysts on the
Hydrogenation and Cracking of Two-Ring
Aromatic and Hydroaromatic Structures Related to Coal

by

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ABSTRACT

An investigation was carried out of the hydrogenation and cracking of two-ring aromatic and hydroaromatic compounds catalyzed by $ZnCl_2$ and $AlCl_3$. The rates of both processes are strongly affected by the Brønsted acidity of the active catalyst [e.g., $H^+(MX_nY)^-$] and the Brønsted basicity of the aromatic portions of the reactant, the latter characteristic being enhanced by either methyl or hydroxyl substitution. The source of hydrogen used for hydrogenation depends on the choice of catalyst. In the presence of $AlCl_3$, Scholl condensation of aromatic nuclei serves as the principle source of hydrogen. Molecular hydrogen is used exclusively, though, when hydrogenation is catalyzed by $ZnCl_2$. The formation of reaction products and the trends in reactant reactivity are discussed on the basis of carbonium ion mechanisms.

INTRODUCTION

It has been proposed (1-7) that Lewis acids participate in the liquefaction of coal by promoting cleavage of the aliphatic, ether, and sulfide linkages present between the aromatic and hydroaromatic portions of the coal structure and by catalyzing the hydrogenation of the aromatic centers. Since the latter function contributes substantially to the consumption of H_2 , it is highly desirable to understand the role of Lewis acids in the hydrogenation of aromatic groups and the influence of substituents attached to such groups on the rate of hydrogenation. Answers to these questions cannot be obtained by working with coal because of its excessively complex structure. However, progress can be made by investigating the reactions of model compounds selected to represent the aromatic portions of coal.

Recent investigations of coal and coal derived liquids (8-11) suggest that the aromatic portions of coal consist of single benzene rings and polycondensed structures containing two or three rings. The ratios of two-ring and three-ring structures to one-ring structures has been estimated to be 0.25 and 0.15, respectively (11). In view of this, benzene, naphthalene, anthracene, and phenanthrene, and derivatives of these compounds, may be considered as models for the aromatic portions of coal, which do not involve heterocycles.

A significant number of studies have been published concerning the hydrogenation and cracking of two and three ring aromatic compounds catalyzed by Lewis acids in the form of metal halides (12-28). In most instances the reactions of these compounds were carried out at temperatures in excess of

400°C and H₂ pressures of 100 to 400 atm. Under such severe conditions extensive hydrogenation and cracking of the original reactant occurs, leading to the observation of a broad spectrum of products, including tar. Because of this, it has been difficult to identify the paths by which reactants are connected to products and the relative rates along competing segments of the reaction network.

The present study was undertaken to develop a better understanding of the role of Lewis acid catalysts in promoting the hydrogenation and cracking of two ring aromatic and hydro-aromatic compounds. More specifically, it was desired to establish the influence of catalyst acidity on the activity and selectivity of Lewis acid catalysts, the sources of hydrogen required for hydrogenation and cracking, and the relationships between reactant structure and reactivity. To pursue these objectives, the reactions of naphthalene, dihydronaphthalene, tetralin, 1-methylnaphthalene, 1-naphthol, 1,2,3,4-tetrahydro-1-naphthol and 5,6,7,8-tetrahydro-1-naphthol were investigated in the presence of both ZnCl₂ and AlCl₃.

EXPERIMENTAL

Apparatus and Procedure

Reaction of the model compounds, dissolved in cyclohexane, was carried out in a glass liner placed inside a stainless steel autoclave (Autoclave Engineers, Inc. Model ABP-300). Details concerning the autoclave and the ancillary equipment, as well as a description of the procedure used to conduct a run may be found in references (5-7).

Following reaction, the products were weighed, and the solid and liquid components were separated by filtration. Quantitative analysis of the liquid products was carried out by gas chromatography, using a 3 mm x 3 m column packed with 5% OV-225 on Chromsorb P. Product identification was established with the aid of a Finnigan 4023 gas chromatograph/mass spectrometer.

Materials

The following compounds were used as reactants: naphthalene (Matheson, Coleman & Bell), 1,2-dihydronaphthalene (Aldrich), tetralin (Baker), 1-methylnaphthalene (Aldrich), 1-naphthol (Aldrich), 1,2,3,4-tetrahydro-1-naphthol (Aldrich), 5,6,7,8-tetrahydro-1-naphthol (Aldrich). All reactants were used as received without further purification. Cyclohexane (Matheson, Coleman & Bell) was used as the solvent in all experiments. This material was spectral quality and was used as received.

Anhydrous AlCl_3 (Mallinkrodt) was used as received and was stored in a dry box under nitrogen to avoid contact with water vapor. Zinc chloride (Mallinkrodt) was dried in a vacuum oven at 110°C and was also stored in the dry box until used.

RESULTS

Product distributions and reactant conversions to products obtained following reaction in the presence of ZnCl_2 are shown in Tables Ia and Ib. Under the conditions used for these experiments, the solvent, cyclohexane, does not react, and none of the substrates are converted to tar.

Naphthalene reacts to only a limited degree (0.6%), forming primarily tetralin and a small amount of dihydronaphthalene, an intermediate product in the hydrogenation of naphthalene. Dihydronaphthalene is very reactive (81% conversion) and undergoes both rapid hydrogenation to form tetralin and, to a lesser degree, dehydrogenation to form naphthalene. Tetralin, the final product of either naphthalene or dihydronaphthalene hydrogenation, is quite stable and reacts to a small extent (1.3% conversion), forming mainly decalin, naphthalene, methylindan, and indan. The absence of significant amounts of alkylbenzenes indicates that under the reaction conditions used tetralin does not undergo extensive cracking of the saturated ring.

The introduction of a nucleophilic substituent enhances the reactivity of naphthalene substantially. As seen in Table Ib the conversion of 1-methylnaphthalene is tenfold greater than that of naphthalene and the conversion of 1-naphthol is over forty times as great. The primary products formed from 1-methylnaphthalene are methyl and dimethyl tetralin. The first of these products results from hydrogenation of the methyl-containing aromatic ring. The second product is formed by disproportionation of methylnaphthalene to form dimethylnaphthalene, followed by hydrogenation of the dimethylated ring. This sequence is supported by the observation of naphthalene and alkylnaphthalenes among the reaction products.

Naphthol reacts to form a variety of products, the principal ones being tetralin, tetralone, naphthalene, 5,6,7,8-tetrahydro-1-naphthol, and dihydronaphthalene. Smaller amounts of 1,2,3,4-tetrahydro-1-naphthol and various alkyl

benzenes are also observed. The formation of both tetrahydro-naphthol isomers suggests that these compounds may be intermediates in the hydrogenation of 1-naphthol, and, as a result, the reactions of these compounds were also investigated. The 5,6,7,8-tetrahydro-1-naphthol reacts to only a limited degree (4% conversion) to form 5,6,7,8-tetrahydro-2-naphthol, 2-naphthol, alkylbenzenes, decalin, tetralin, and a variety of other products in smaller yield. The reaction of 1,2,3,4-tetrahydro-1-naphthol is much more extensive (80% conversion). The principal products in this case are tetralin and naphthalene. Small amounts of 1-naphthol, 5,6,7,8-tetrahydro-2-naphthol, dihydronaphthalenes, and alkylbenzenes are also observed.

Tables IIa and IIb show product distributions and conversions of reactants to products obtained when AlCl_3 is used as the catalyst. Also shown are the products obtained in a blank run in which only cyclohexane and AlCl_3 were present. As can be seen, the solvent reacts extensively to form methylcyclopentane and smaller amounts of alkanes, alkylcyclohexanes, benzene, and alkylbenzenes. A small amount of tar is also formed. In the presence of an aromatic reactant the reactions of cyclohexane are suppressed due to the fact that the catalyst interacts more strongly with the reactant than with the solvent. However, the degree of cyclohexane reaction which still occurs is sufficient to make it impossible to distinguish between the alkylbenzenes resulting from the reactants as opposed to cyclohexane. As a result, the indicated conversions of substrate to alkylbenzenes represent an upper limit.

Virtually the same liquid products are obtained using AlCl_3 as the catalyst as are obtained using ZnCl_2 . The principal difference is that, in general, higher conversions are obtained with AlCl_3 . Thus, for example, the conversion of naphthalene to tetralin is 17% in the presence of AlCl_3 but only 0.5% in the presence of ZnCl_2 . The extent of cracking and tar formation are also significantly greater with AlCl_3 . This trend is most evident in the case 5,6,7,8-tetrahydro-1-naphthol, where interference from the products of cyclohexane reaction is limited. In the presence of ZnCl_2 , 1.3% of the 1-naphthol is converted to alkylbenzenes. On the other hand, cracking in the presence of AlCl_3 results in a 2.1% conversion to alkylphenols and a 4% conversion to alkylbenzenes. The effect of catalyst composition on the extent of tar formation is even more dramatic, no tar being observed in the presence of ZnCl_2 but conversion to tar as high as 80% being found in the presence of AlCl_3 .

To establish the extent to which molecular H_2 is involved in the hydrogenation and cracking of two-ring aromatic compounds, experiments were carried out with 1-naphthol, using N_2 to pressurize the autoclave. The results, shown in Tables IIIa and IIIb, demonstrate that the effects of gas composition on the extent of 1-naphthol reaction and the distribution of products depend strongly on whether ZnCl_2 or AlCl_3 is used as the catalyst. In the presence of ZnCl_2 , the conversion of 1-naphthol to liquid products is 4% when the autoclave is pressurized with N_2 as opposed to 25% when using H_2 . While some tetralone and naphthalene are formed in the absence of H_2 ,

the formation of dihydronaphthalene and tetralin are greatly suppressed. It is also noted that while no tar is formed in the presence of H_2 , 77% of the 1-naphthol is converted to tar in the absence of H_2 . When $AlCl_3$ is used as the catalyst, the results presented in Table IIIb show that gas composition has virtually no effect on product composition. Based on these results it is concluded that molecular H_2 provides a major portion of the hydrogen required for the hydrogenation of 1-naphthol when it is catalyzed by $ZnCl_2$. But when this reaction is catalyzed by $AlCl_3$, Scholl condensation of 1-naphthol to tar provides the primary source of hydrogen.

DISCUSSION

Structure of the Active Catalyst

In the field of Friedel-Crafts chemistry it is generally accepted that Lewis acids become active catalysts when converted to their Brønsted acid form (29-32). This conversion is envisioned to occur via a reaction of the Lewis acid with hydrogen halide, water, or an alcohol. Thus, it has been observed that anhydrous, freshly sublimed, $AlCl_3$ fails to initiate many Friedel-Crafts reactions without the addition of H_2O or HCl as promoters (30-32). The activity of $ZnCl_2$ is also enhanced by the presence of H_2O (22,30). Since the present work was not carried out under completely anhydrous conditions, it is likely that the active catalyst were species such as $H^+(ZnCl_2OH)^-$ (33), $H^+(AlCl_3OH)^-$, or $H^+(AlCl_4)^-$ (30,32). Based on these considerations, the active form of the catalyst will be designated as $H^+(MX_nY)^-$ for the purposes of subsequent discussion.

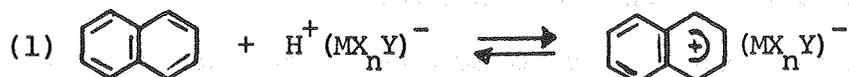
Hydrogenation and Cracking of Naphthalene, Dihydronaphthalene, and Tetralin

Figure 1 illustrates a possible reaction sequence for the hydrogenation and cracking of naphthalene, which is deduced from the products observed following the reaction of naphthalene, dihydronaphthalene, and tetralin in the presence of $ZnCl_2$ and $AlCl_3$. This sequence involves stepwise hydrogenation of naphthalene to dihydronaphthalene and tetralin, followed by further hydrogenation of tetralin to decalin, or cracking of tetralin to form alkylbenzenes. The last step may occur directly or through methylindan and indan. Reaction sequences similar to that given in Fig. 1 have been proposed for the hydrogenation and cracking of naphthalene in the presence of solid acids (34) and the strong acid system HF/TaF_5 (35).

A feeling for the relative rates of the individual reactions shown in Fig. 1 can be established by examination of Tables I and II. As was noted earlier, naphthalene undergoes hydrogenation very slowly. On the other hand, dihydronaphthalene is very reactive and is converted to both tetralin and naphthalene in high yield. This indicates that the hydrogenation of naphthalene to dihydronaphthalene (reaction 1) is slower than the reverse reaction (reaction-1). It should be noted, however, that the hydrogenation of dihydronaphthalene also occurs very rapidly, and that, in fact, the rate of hydrogenation (reaction 2), is more rapid than the rate of dehydrogenation (reaction-1), as evidenced by the threefold higher conversion of dihydronaphthalene to tetralin than to naphthalene. Tetralin is not very reactive under the conditions noted in Tables I and II, and only small conversions are observed to decalin,

methylindan, indan, alkylbenzenes, and naphthalene. This indicates that reactions 2, and 3 through 8 are relatively slow. The relative rates of tetralin hydrogenation and cracking could not be established in the present work. However, when naphthalene and tetralin are reacted at 425°C (36), alkylbenzenes are observed as the final products rather than decalin, suggesting that the rates of reactions 4 and 5 are higher than the rate of reaction 3.

The hydrogenation and cracking of naphthalene can be envisioned to proceed via a cationic mechanism. In the first step of the sequence naphthalene is protonated by the Brønsted acid form of the catalyst to yield a naphthalenium ion (35,37-41). This process is illustrated by reaction 1.

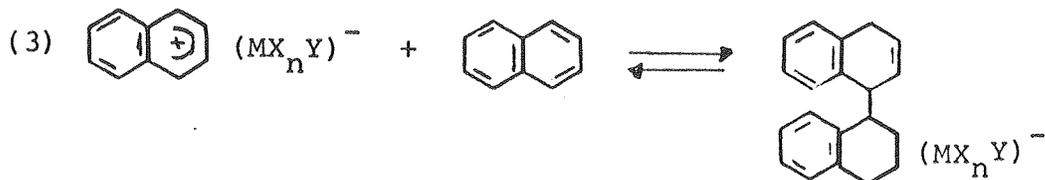


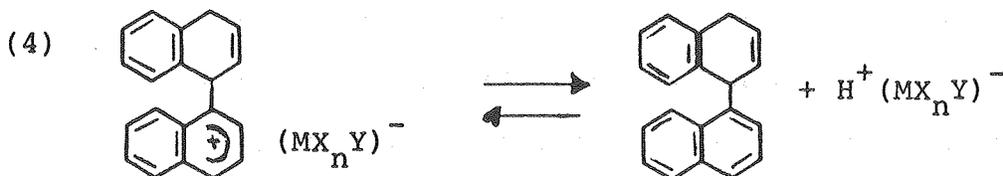
It should be noted that the naphthalenium cation very likely remains in association with the $(\text{MX}_n\text{Y})^-$ anion since the dielectric coefficient of the solvent, cyclohexane, is low.

The ion pair formed in reaction 1 can react with either a hydride source to form dihydronaphthalene,



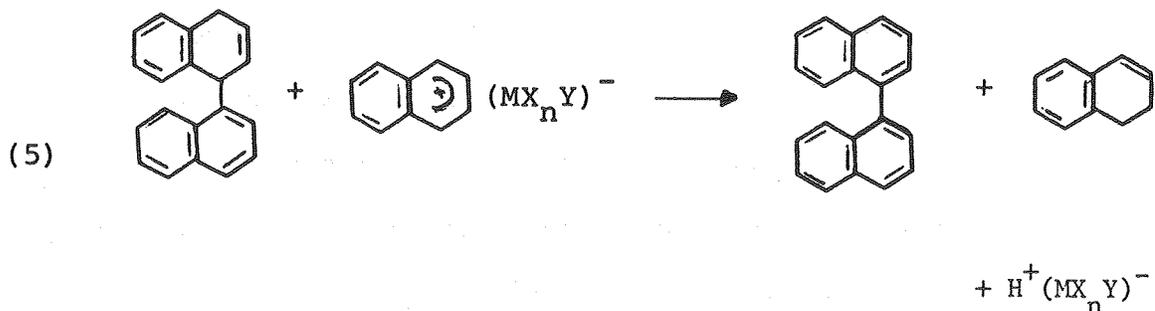
or with a molecule of naphthalene to form dihydrobinaphthyl via Scholl condensation (42,43).



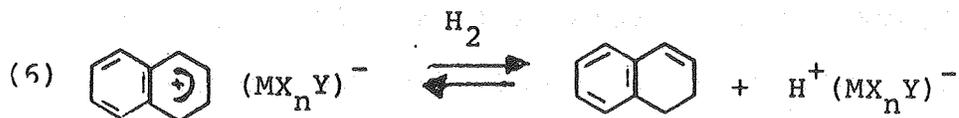


The occurrence of the latter process is undesirable since it initiates a sequence of reactions which ultimately leads to the formation of a highly aromatic tar. The extent to which Scholl condensation takes place depends on the acidity of the catalyst and the basicity of the aromatic nuclei present in solution. The Brønsted acid form of a strong Lewis acid such as AlCl_3 is more acidic than that for a weaker Lewis acid such as ZnCl_2 (44). As a consequence, the concentration of protonated naphthalene is higher in the presence of AlCl_3 than ZnCl_2 . It is also expected that the degree of charge separation between the partners of the anion/cation pair formed from naphthalene and the Brønsted acid form of the catalyst in reaction 1 will be greater when AlCl_3 is used as the catalyst. Both of these factors are known to enhance the rate at which Scholl condensation occurs (43).

The hydride ion required to form dihydronaphthalene can come from two sources. The first is hydride transfer from a hydrocarbon species. One source of such ions is the initial product formed during Scholl condensation, dihydrobinaphthyl (27). The reaction of this product might be envisioned to proceed as follows



The results presented in Table III clearly demonstrate that this is the primary source of hydride ions when AlCl₃ is used as the catalyst. Methylcyclopentane formed by the isomerization of cyclohexane in the presence of AlCl₃ might also be envisioned as a tertiary hydride donor (35,45); however, this mechanism does not seem to be operative, since the addition of methylcyclopentane to the reactants in the presence of AlCl₃ has no effect on the product distribution (36). The second source of hydride ions is molecular H₂.



The results presented in Table III indicate that H₂ is the primary source of hydride ions when ZnCl₂ is used as the catalyst. Presumably, H₂ dissociation is accomplished by coordination of molecular hydrogen to the cation/anion pair during the first stage of reaction 6.

The hydrogenation of dihydronaphthalene to tetralin very likely proceeds via stepwise protonation and hydride abstraction, in a manner similar to that shown for naphthalene. In the event that hydride abstraction occurs first, then dihydronaphthalene will undergo dehydrogenation to form naphthalene, i.e., the reverse of reactions 6 and 1.

The reactivity of tetralin to hydrogenation is significantly lower than that of naphthalene due to the presence of only a single phenyl ring and, consequently, a lower basicity. The mechanism of tetralin hydrogenation to decalin, however, is expected to proceed in essentially the same manner as the hydrogenation of naphthalene to tetralin. Failure to observe any dihydrotetralin suggests that once formed this compound is highly reactive and readily adds additional hydrogen to form decalin.

In the discussion of Fig. 1 it was noted that tetralin will isomerize to methylindan and crack to a variety of alkylbenzenes. The mechanism by which these products are formed is undoubtedly complex and may involve a large number of intermediates. A plausible reaction network for the formation of at least some of the observed products is illustrated in Fig. 2. This scheme, which is based upon studies of tetralin isomerization and cracking over solid acid catalysts (46), initiates with either protonation at the 9(10)-position or abstraction of a hydride ion at the 5(8)-position of tetralin. The subsequent rearrangement of the primary cations follows the rules governing the reactions of carbonium ions.

Hydrogenation and Cracking of Methyl-naphthalene

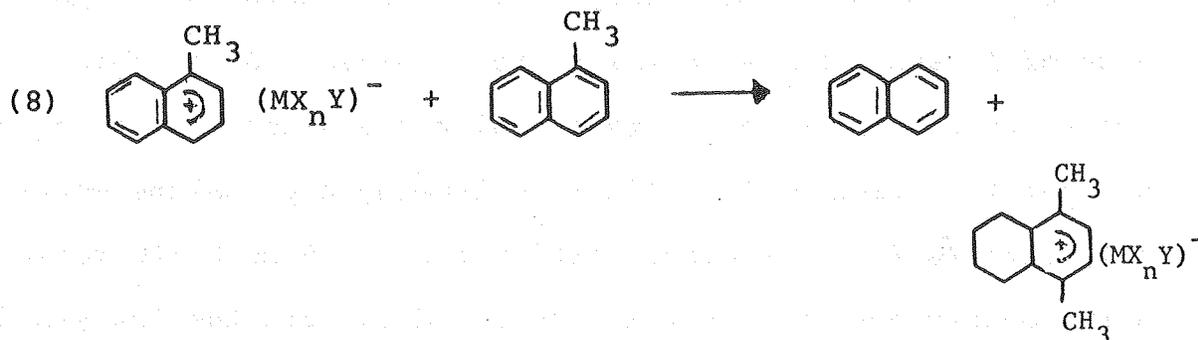
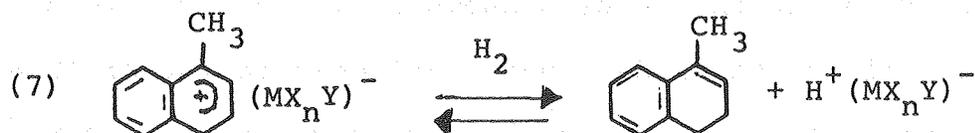
A possible reaction sequence for the hydrogenation and

cracking of 1-methylnaphthalene is presented in Fig. 3. Disproportionation of 1-methylnaphthalene results in the formation of naphthalene, which in turn can undergo hydrogenation to form tetralin. Both 5-methyltetralin and 1-methyltetralin are produced by hydrogenation of 1-methylnaphthalene. The 5-methyltetralin can disproportionate to form tetralin and both isomers of methyltetralin can crack to form alkylbenzenes. The results presented in Tables I and II show that only small amounts of naphthalene and methylnaphthalenes are formed compared to methyltetralin and tetralin, indicating that reaction 2 and 3 are significantly faster than reaction 1. The relative rates of reactions 2 and 3 are harder to establish. Based on the results shown in Table I obtained with $ZnCl_2$ it would be concluded that reaction 3 is faster than reaction 2, since only 1-methyltetralin is observed. However, when $AlCl_3$ is used as the catalyst, Table II shows that comparable yields of 1- and 5-methyltetralin are obtained. Since the hydrogenation of naphthalene to tetralin has been found to be very slow, the formation of tetralin from 1-methylnaphthalene most likely derives from the disproportionation of 5-methyltetralin, and the occurrence of this reaction could explain the low yields of 5-methyltetralin observed with $ZnCl_2$. The presence of only small amounts of tetralin among the products makes it unlikely that the observed yields of alkylbenzenes derive from tetralin. A more probable interpretation is that the alkylbenzenes are obtained by cracking of 1- and 5-methyltetralin.

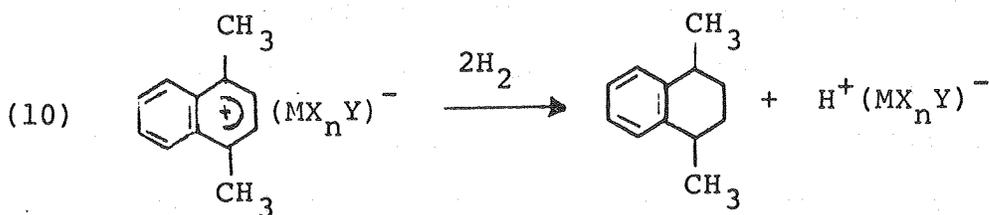
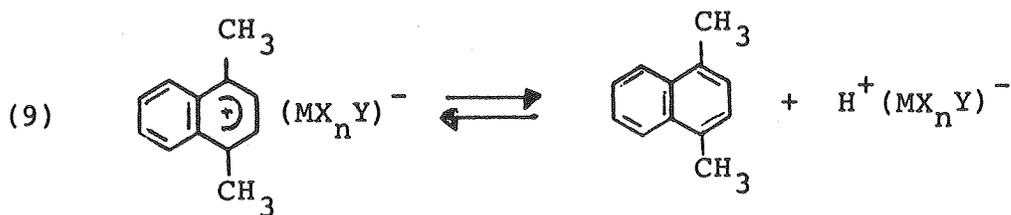
The higher reactivity of 1-methylnaphthalene relative to naphthalene can be ascribed to the higher basicity of the former compound. Studies performed with HF indicate that the pK_B for

protonation of the 4-position of 1-methylnaphthalene is 4.0 while that for the protonation of the 1-position of naphthalene is 1.7 (37). Because of the high value of pK_B , the equilibrium concentration of anion/cation pairs, formed by protonation 1-methylnaphthalene, is high and this in turn accelerates the rate of subsequent reactions.

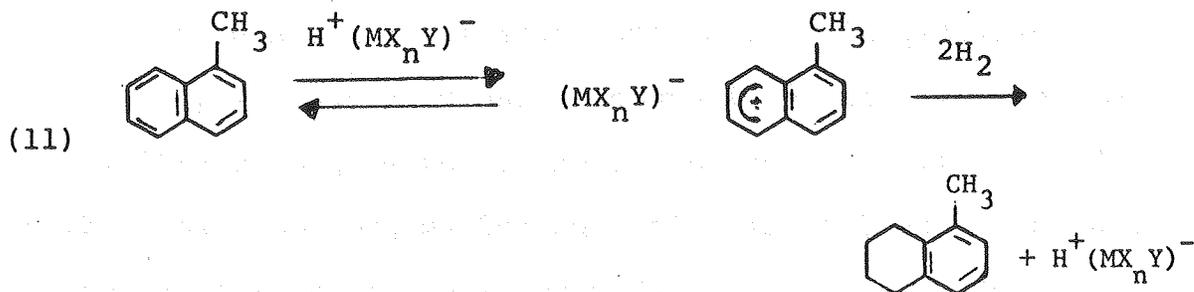
The protonated form of 1-methylnaphthalene can either accept a hydride ion or transfer a methyl carbonium ion to another molecule of 1-methylnaphthalene, as illustrated by reactions 7 and 8.



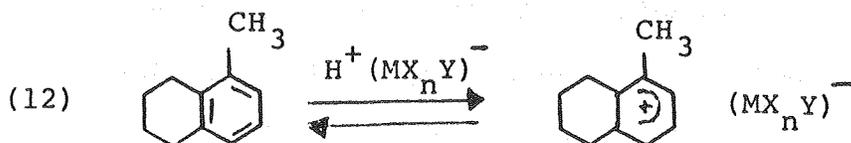
The dihydro-1-methylnaphthalene produced in reaction 7 is not observed experimentally and is, therefore, presumed to undergo rapid hydrogenation to 1-methyltetralin, in a manner analogous to that noted earlier for dihydronaphthalene. The 1,4-dimethylnaphthalenium cation formed in reaction 8 may either lose a proton or accept a hydride ion and add an additional molecule of H_2 . These reactions can be represented as

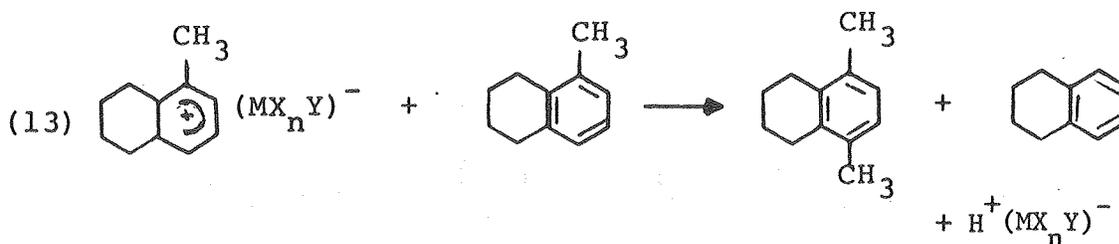


While protonation of 1-methylnaphthalene at the 4-position is preferred, protonation can also occur at the 8-position, resulting ultimately in the formation of 5-methyltetralin.



The 5-methyltetralin formed in reaction 11 can produce tetralin as a result of protonation followed by transfer of a methyl carbonium ion to another aromatic center. This sequence is exemplified by reactions 12 and 13.





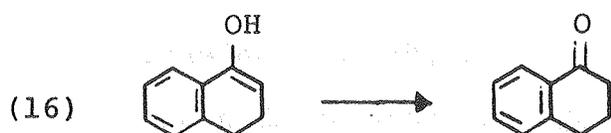
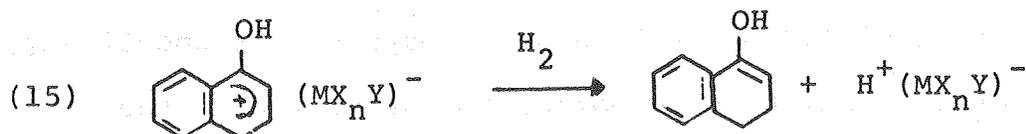
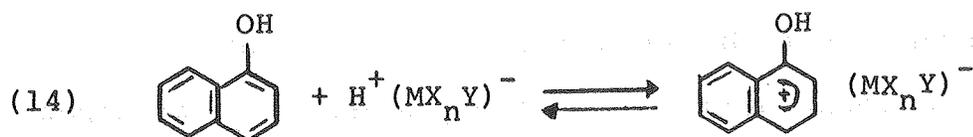
The cracking of 1- and 5-methyltetralin as well as 1,5-dimethyltetralin is very likely initiated by protonation of the aromatic ring in a manner similar to that shown for tetralin in Fig. 2. Since the presence of methyl groups enhances the basicity of the ring, the concentration of the protonated form of the reactant would be expected to increase with an increase in the number of methyl groups present on the ring. Following this reasoning, the cracking of 1-methyltetralin should occur more readily than the cracking of 5-methyltetralin. This tendency might be balanced, though, by the fact that a secondary carbonium ion is formed upon cleavage of the saturated ring of 5-methyltetralin while a primary carbonium is formed by cleavage of the saturated ring of 1-methyltetralin. Since the first of these species will be more stable, its formation is expected to proceed more readily than the formation of the latter species. In view of these considerations, it is possible that both isomers of methyltetralin undergo cracking at nearly equivalent rates.

Hydrogenation and Cracking of Naphthol and Tetrahydronaphthol

Figure 4 illustrates the sequence of reactions believed to occur during the hydrogenation and cracking of 1-naphthol. The hydrogenation of both rings can occur, leading to the formation of 1,2,3,4- and 5,6,7,8-tetrahydro-1-naphthol.

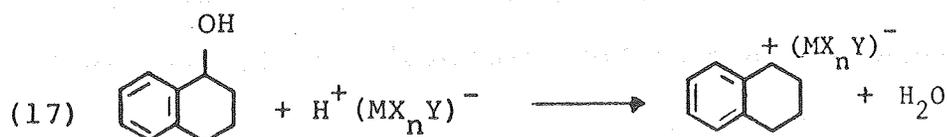
Tetralone is assumed to be an intermediate along the path to the first of these products. The appearance of significant yields of tetralin and dihydronaphthalene among the reaction products of 1-naphthol can be ascribed to the dehydroxylation and dehydration of 1,2,3,4-tetrahydro-1-naphthol, respectively, an interpretation which is supported by inspection of the products derived from the reaction of 1,2,3,4-tetrahydro-1-naphthol itself. Consistent with this view, naphthalene is formed via the dehydrogenation of dihydronaphthalene. Examination of Tables I and II suggests that decalin and various alkyl phenols are formed via the reaction of 5,6,7,8-tetrahydro-1-naphthol and it is observed that the yield of decalin is much higher than that obtained by reaction of tetralin. Tables I and II also show that 5,6,7,8-tetrahydro-1-naphthol can isomerize to form 5,6,7,8-tetrahydro-2-naphthol and that this product can in turn form 2-naphthol. Since the yields of 1,2,3,4-tetrahydro-1-naphthol and the products derived from it are substantially higher than the yield of 5,6,7,8-tetrahydro-1-naphthol and the products derived from it, it is concluded that reaction 2 is faster than reaction 1.

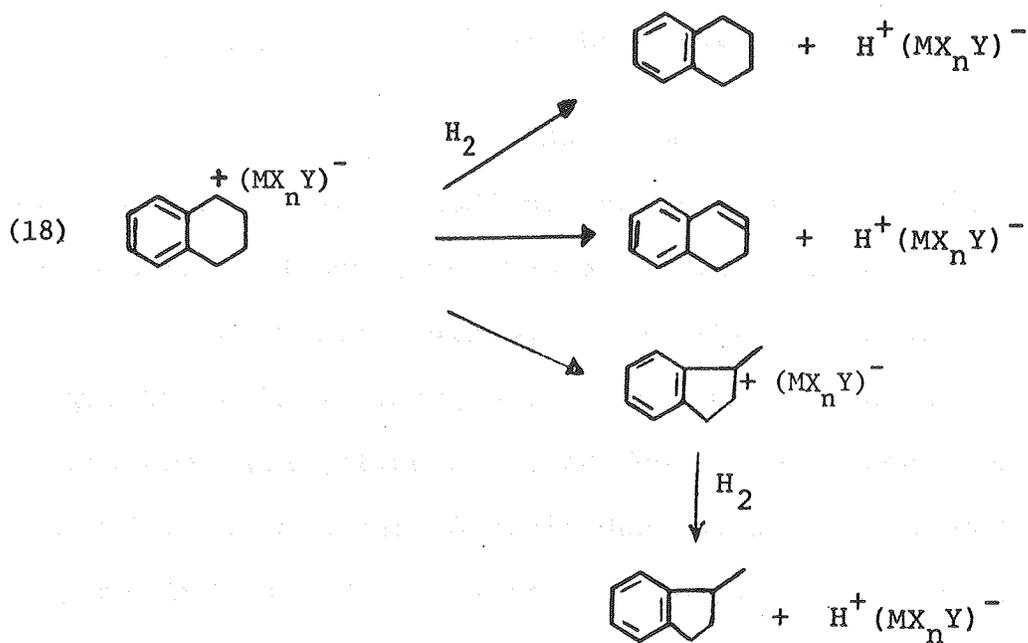
The hydrogenation of 1-naphthol is assumed to proceed via a mechanism analogous to that proposed earlier for naphthalene and 1-methylnaphthalene. The higher reactivity of 1-naphthol can be ascribed to the strong electron-releasing characteristic of the -OH group (37). Protonation will occur preferentially at the 4-position and is rapidly followed by hydride acceptance and an enol-keto conversion (47), reactions 14-16.



The tetralone produced in reaction 16 can then undergo further hydrogenation to form 1,2,3,4-tetrahydro-1-naphthol. The hydrogenation of 1-naphthol to form 5,6,7,8-tetrahydro-1-naphthol is envisioned to proceed via a similar mechanism, with the exception that an enol is not formed as an intermediate.

Protonation of the oxygen in 1,2,3,4-tetrahydro-1-naphthol produces a tetralenium ion which can undergo one of three possible reactions: hydride acceptance to form tetralin; proton elimination to form dihydronaphthalene; or isomerization followed by hydride acceptance to form methylindan. This portion of the mechanism is summarized by reactions 17 and 18.





Of the three products formed in reaction 18, dihydronaphthalene is the most reactive. As discussed earlier, this compound can undergo either hydrogenation to form tetralin or dehydrogenation to form naphthalene.

Figure 4 shows that 5,6,7,8-tetrahydro-1-naphthol reacts to form decalin and a variety of alkylphenols and alkylbenzenes. The mechanism for decalin formation is assumed to be similar to that proposed for the hydrogenation of 1-naphthol to 1,2,3,4-tetrahydronaphthol and the conversion of the latter product to tetralin, reactions 14-18. Cracking of the saturated ring of 5,6,7,8-tetrahydro-1-naphthol resembles the cracking of tetralin, but occurs to a larger extent, very likely because of the presence of the electron-releasing OH group on the aromatic ring. The alkylphenol formed immediately upon cracking of the saturated ring may undergo subsequent dealkylation to produce phenol or react with naphthalene to

produce phenol and an alkylnaphthalene. The details of these latter processes are not well understood at present.

CONCLUSIONS

The present investigation has shown that the hydrogenation and cracking of two-ring aromatic and hydroaromatic structures catalyzed by $ZnCl_2$ and $AlCl_3$ are strongly influenced by nucleophilic substitution of the rings. The presence of a hydroxyl group at the 1-position of naphthalene greatly increases the rate of hydrogenation of the substituted ring and, to a lesser degree, the neighboring ring. Substitution of a methyl group at the 1-position causes a somewhat smaller increase in the rate of hydrogenation of naphthalene, but in this case both rings are affected to nearly an equivalent extent. Cracking of the saturated ring in tetralin is also enhanced by substitution of either a methyl or a hydroxyl group on the unsaturated ring.

It has also been demonstrated that $ZnCl_2$ and $AlCl_3$ will promote two other types of reaction, in addition to hydrogenation and cracking. The first, is the removal of nucleophilic substituents. In the case of substitution by methyl groups, this occurs by disproportionation and is exemplified by the reaction of 1-methylnaphthalene to form naphthalene and dimethylnaphthalene. In the case of hydroxyl groups, substituent removal occurs by dehydration as illustrated by the conversion of 1-naphthol to 1,2,3,4-tetrahydro-1-naphthol and the subsequent reaction of this product to produce

dihydronaphthalene and water. The second type of reaction is Scholl condensation to produce an aromatic tar. Under the reaction conditions used in these studies, this process is only observed using AlCl_3 as the catalyst.

Finally, it has been concluded that the observed products and trends in reactant reactivity can be explained on the basis of a carbonium ion mechanism. In this scheme the active catalyst is a Brønsted acid represented by $\text{H}^+(\text{MX}_n\text{Y})^-$ [$\text{M} = \text{Zn, Al}$; $\text{X} = \text{Cl}$; $\text{Y} = \text{OH, Cl}$]. Hydrogenation is proposed to occur via sequential protonation and hydride acceptance. The first of the steps involves the transfer of a proton from the active catalyst to the substrate, a process which is enhanced by the presence of a nucleophilic substituent on the aromatic portion of the reactant. The second step proceeds by transfer of a hydride ion from one of the products of Scholl condensation or from molecular hydrogen. The first of these two sources is predominant when AlCl_3 is used as the catalyst and the second when ZnCl_2 is used. The cracking of hydroaromatic rings is initiated by either protonation or hydride abstraction and then progresses through a complex series of ionic reactions.

ACKNOWLEDGMENTS

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Table Ia

Concentrations of Reaction Products Obtained from
Two-Ring Compounds in the Presence of $ZnCl_2$

Reaction Conditions: Solvent = Cyclohexane. Reactant concentration = 2.0-2.2 mole%;
mole $ZnCl_2$ /mole reactant = 0.54; T = 325°C; P (H_2 , at 25°C) = 600 psig;
P (at T) = 1600 psig; t = 1 hr at T.

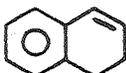
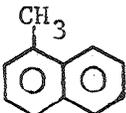
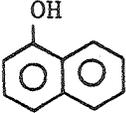
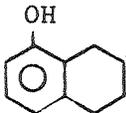
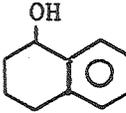
Reactant							
Products	C,wt%	C,wt%	C,wt%	C,wt%	C,wt%	C,wt%	C,wt%
cyclohexane	96.7	96.7	99.6	99.6	98.4	97.9	97.4
toluene	-	0.001	0.001	0.001	0.002	0.005	0.009
o-xylene	-	-	-	0.003	-	-	-
ethylbenzene	-	-	trace	0.001	-	-	0.001
propylbenzene & isomers	-	-	-	-	trace	0.015	-
decalin	-	-	0.018	-	-	0.017	-
indan	-	0.001	0.005	-	-	-	0.002
methylindans	-	0.004	0.002	0.001	0.001	0.018	0.006
tetralin	0.017	2.09	3.34	0.034	0.45	0.013	2.07
dihydronaphthalene	0.002	0.45	-	0.002	0.069	-	0.016
1-methyltetralin	-	-	-	0.091	-	-	-
naphthalene	3.28	0.65	0.012	0.008	0.10	0.001	0.37
dimethyltetralin	-	-	-	0.040	-	-	-
1,2,3,4-tetrahydro-1-naphthol	-	-	-	-	0.006	0.001	0.008
1-methylnaphthalene	trace	0.021	-	3.15	-	0.001	trace
1-tetralone	-	-	-	-	0.13	0.001	trace
other alkylnaphthalenes	-	-	0.003	0.009	-	-	-
5,6,7,8-tetrahydro-1-naphthol	-	-	-	-	0.074	1.94	0.026
5,6,7,8-tetrahydro-2-naphthol	-	-	-	-	-	0.046	-
1-naphthol	-	-	-	-	0.080	-	0.035
2-naphthol	-	-	-	-	-	0.046	-

Table Ib

Conversions of Two-Ring Compounds to Products in the Presence of ZnCl₂Reaction Conditions: Same as Table Ia

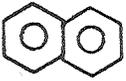
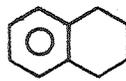
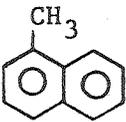
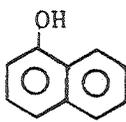
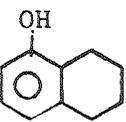
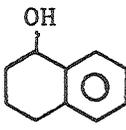
Reactant							
<u>Reactant to Products</u>	<u>X,mole%</u>	<u>X,mole%</u>	<u>X,mole%</u>	<u>X,mole%</u>	<u>X,mole%</u>	<u>X,mole%</u>	<u>X,mole%</u>
total	0.6	81	1.3	6	25	4	80
alkylbenzenes and indans	-	0.2	0.2	0.3	0.1	1.3	0.6
decalin	-	-	0.6	-	-	0.5	-
tetralin	0.5	61	(99)	1.1	14	0.4	66
methyl- and dimethyltetralin	-	-	-	3.6	-	-	-
dihydronaphthalene	0.06	(16)	-	0.07	2.1	-	0.5
naphthalene	(96)	19	0.4	0.25	3.4	0.03	12
1-methylnaphthalene	-	-	-	(92)	-	0.02	-
other alkyl naphthalenes	-	0.5	0.1	0.4	-	-	-
1-tetralone	-	-	-	-	3.5	0.01	-
1,2,3,4-tetrahydro-1-naphthol	-	-	-	-	0.1	0.01	(trace)
5,6,7,8-tetrahydro-1-naphthol	-	-	-	-	2.1	(sat.)	0.7
5,6,7,8-tetrahydro-2-naphthol	-	-	-	-	-	1.4	-
1-naphthol	-	-	-	-	(sat.)	-	1.0
2-naphthol	-	-	-	-	-	1.4	-

Table IIa

Concentrations of Reaction Products Obtained from
Two-Ring Compounds in the Presence of AlCl₃

Reaction Conditions: Solvent = Cyclohexane; Reactant concentration = 2.0-2.2 mole %;
 mole AlCl₃/mole reactant = 0.54; T = 325°C; P(H₂, at 25°C) = 600 psig;
 P (at T) = 1600 psig; t = 1 hr at T

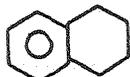
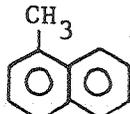
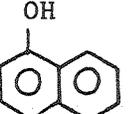
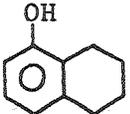
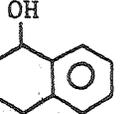
Reactant								
Products	C,wt%	C,wt%	C,wt%	C,wt%	C,wt%	C,wt%	C,wt%	C,wt%
alkanes	7.95	1.29	2.32	2.47	1.30	0.033	0.030	0.13
methylcyclopentane	44.1	11.5	15.2	34.6	11.5	1.49	1.30	0.32
cyclohexane	36.1	84.0	78.6	56.8	83.8	97.8	97.2	97.3
methylcyclohexane	3.88	0.40	0.86	1.52	0.65	-	-	-
benzene	2.33	0.46	0.88	1.54	0.50	0.004	-	0.034
ethylcyclohexane	0.96	0.075	0.16	0.36	0.14	0.016	-	-
propylcyclohexane	1.11	0.035	-	-	-	-	0.001	-
toluene	0.70	0.11	0.30	0.45	0.22	0.016	-	0.011
ethylbenzene	-	0.082	0.23	0.39	-	0.004	0.010	0.004
hydrindan	-	-	-	-	-	-	0.036	-
o-xylene	0.44	0.015	0.042	0.065	0.15	0.001	-	0.002
propylbenzene/decalin	0.14	0.022	-	-	0.030	-	0.044	-
methylethylbenzene/decalin	-	0.037	0.096	0.19	0.073	0.001	0.079	0.002
trimethylbenzene	0.31	0.028	0.44	-	-	-	-	-
butylbenzene	0.46	-	-	0.19	-	0.015	-	0.003
propenylbenzene	-	0.095	0.16	0.34	-	-	-	-
diethylbenzene	0.55	0.018	-	0.90	-	0.010	-	0.001
indan	0.32	0.070	0.10	0.18	0.10	0.005	0.009	0.003
indene	0.46	-	-	-	0.094	-	-	-
methylindans	0.23	0.13	0.18	0.12	0.18	0.009	0.015	0.008
tetralin	-	0.59	0.47	0.23	0.071	0.11	0.46	1.70
dihydronaphthalene	-	0.020	0.013	0.035	-	0.008	-	0.001
1-methyltetralin	-	0.040	0.044	0.076	0.17	-	-	-
naphthalene	-	0.63	0.13	0.081	0.12	0.13	0.10	0.44
phenol	-	-	-	-	-	-	0.002	-
5-methyltetralin	-	0.016	0.011	0.023	0.17	0.002	-	-

Table IIa (continued)

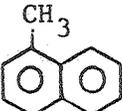
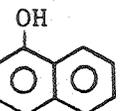
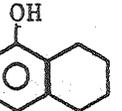
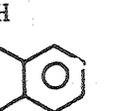
Reactant														
	Products	C,wt%	C,wt%	C,wt%	C,wt%	C,wt%	C,wt%	C,wt%	C,wt%	C,wt%	C,wt%	C,wt%	C,wt%	C,wt%
dimethyltetralin	-	0.011	0.006	0.020	-	-	-	-	-	-	-	-	-	-
1,2,3,4-tetrahydro-1-naphthol	-	-	-	-	-	-	trace	-	-	-	-	-	trace	-
1-methylnaphthalene	-	0.076	0.031	0.035	0.15	0.003	0.009	0.003	0.009	0.009	0.009	0.009	0.003	0.003
2-methylnaphthalene	-	0.030	0.009	0.015	0.009	0.002	-	-	-	-	-	-	-	-
dimethylnaphthalene/biphenyl	-	0.073	0.019	0.036	0.15	0.006	-	-	-	-	-	-	0.002	-
trimethylnaphthalene	-	-	-	-	0.24	-	-	-	-	-	-	-	-	-
tetramethylnaphthalene	-	-	-	-	0.056	-	-	-	-	-	-	-	-	-
1-tetralone	-	-	-	-	-	0.070	-	0.016	0.016	0.016	0.016	0.016	-	-
propenylphenol	-	-	-	-	-	-	-	0.033	0.033	0.033	0.033	0.033	-	-
butenylphenol	-	-	-	-	-	-	-	0.030	0.030	0.030	0.030	0.030	-	-
5,6,7,8-tetrahydro-1-naphthol	-	-	-	-	-	-	0.003	0.38	0.38	0.38	0.38	0.38	0.016	0.016
5,6,7,8-tetrahydro-2-naphthol	-	-	-	-	-	-	-	0.25	0.25	0.25	0.25	0.25	-	-
higher alkyl naphthalenes	-	0.036	-	-	-	-	0.011	-	-	-	-	-	0.002	0.002
1-naphthol	-	-	-	-	-	-	0.20	-	-	-	-	-	-	-
wt% to tar	0.4	1.2	1.3	1.3	0.9	-	-	-	-	-	-	-	-	-

Table IIb

Comparison of Two-Ring Compounds to Products in the Presence of AlCl₃

Reaction Conditions: Same as for Table IIa

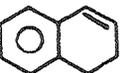
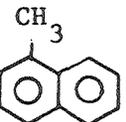
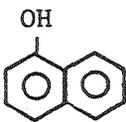
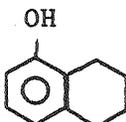
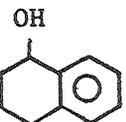
Reactant								
Reactant to Products	X, mole%	X, mole%	X, mole%	X, mole%	X, mole%	X, mole%	X, mole%	X, mole%
total	-	81	97	93	96	94	89	100
decalin	-	-	3	6	3	trace	4	-
tetralin	-	17	13	(7)	2.1	3.4	15	55
dihydronaphthalene	-	0.6	(0.4)	1.0	-	0.3	-	trace
alkyltetralins	-	1.7	1.5	3.1	9.2	trace	-	-
naphthalene	-	(19)	3.7	2.5	3.6	4.2	3.4	15
1-methylnaphthalene	-	2.1	0.8	1.0	(4.2)	0.1	0.3	0.1
other alkylnaphthalenes	-	3.3	0.6	1.3	3.0	0.5	-	-
biphenylalkanes	-	-	-	-	9.1	-	-	-
alkylphenols	-	-	-	-	-	-	2.1	-
1-tetralone	-	-	-	-	-	2.0	0.5	-
1,2,3,4-tetrahydro-1-naphthol	-	-	-	-	-	trace	trace	trace
5,6,7,8-tetrahydro-1-naphthol	-	-	-	-	-	0.1	(11)	0.5
5,6,7,8-tetrahydro-2-naphthol	-	-	-	-	-	-	7.3	-
1-naphthol	-	-	-	-	-	(5.7)	-	-
tar & alkylbenzenes	-	56	77	84	64	84	56	30
(maximum alkylbenzenes)	-	(44)	(84)	(100)	(54)	(3)	(4)	(3)

Table IIIa

Source of Hydrogen in Reaction of 1-Naphthol in Cyclohexane in the Presence of ZnCl₂

Reaction Conditions: Solvent = Cyclohexane; Reactant concentrations = 2.0 mole%;
mole catalyst naphthol = 0.54; T = 325°C; P (at 25°C) = 600 psig;
P (at T) = 1600 psig; t = 1 hr at T.

Catalyst	ZnCl ₂	ZnCl ₂	AlCl ₃	AlCl ₃
Gas	H ₂	N ₂	H ₂	N ₂
<u>Reactant to Products</u>	<u>C,wt%</u>	<u>C,wt%</u>	<u>C,wt%</u>	<u>C(wt%)</u>
alkanes	-	-	0.033	0.035
methylcyclopentane	-	-	1.490	0.320
cyclohexane	98.4	99.4	97.8	98.6
benzene	-	-	0.004	0.031
ethylcyclohexane	-	-	0.016	-
toluene	0.002	0.001	0.016	0.043
ethylbenzene	-	-	0.004	0.005
o-xylene	-	-	0.001	-
methylethylbenzene	-	-	0.001	-
butylbenzene	-	-	0.015	0.008
diethylbenzene	-	-	0.010	0.005
indan	-	-	0.005	0.011
methylindans	0.001	-	0.009	0.010
tetralin	0.450	0.004	0.110	0.094
dihydronaphthalene	0.069	0.005	0.008	0.005
naphthalene	0.105	0.050	0.130	0.180
4-methyltetralin	-	-	0.002	-
1-methylnaphthalene	-	-	0.003	0.052
2-methylnaphthalene	-	-	0.002	0.002
ethylnaphthalene	-	-	0.006	0.009
higher alkylnaphthalenes	-	-	0.011	0.003
1-tetralone	0.130	0.056	0.070	0.059
1,2,3,4-tetrahydro-1-naphthol	0.006	trace	trace	trace
5,6,7,8-tetrahydro-1-naphthol	0.074	trace	0.003	0.004
1-naphthol	0.800	0.650	0.200	0.470
2-naphthol	-	0.010	-	-
wt% to tar	-	-	-	0.5

Table IIIb

Effects of Gas Composition on the Conversion of Naphthol to Products in the Presence of $ZnCl_2$ and $AlCl_3$

Reaction Conditions: Same as for Table IIIa

Catalyst	$ZnCl_2$	$ZnCl_2$	$AlCl_3$	$AlCl_3$
Gas	H_2	N_2	H_2	N_2
<u>Naphthol to Products</u>	<u>X(mole %)</u>	<u>X(mole %)</u>	<u>X(mole %)</u>	<u>X(mole %)</u>
total	25	4	94	87
tetralin	14.0	0.1	3.4	2.9
alkyltetralins	-	-	trace	-
dihydronaphthalene	2.1	0.2	0.3	0.2
naphthalene	3.4	1.6	4.2	5.7
alkylnaphthalenes	-	-	0.6	0.4
1-tetralone	3.5	1.6	2.0	1.6
1,2,3,4-tetrahydro-1-naphthol	0.1	trace	trace	trace
5,6,7,8-tetrahydro-1-naphthol	2.1	trace	0.1	0.1
2-naphthol	-	0.3	-	-
tar & alkylbenzenes	0.1	77	84	76

FIGURE CAPTIONS

- Fig. 1 Proposed sequence for the hydrogenation and cracking of naphthalene
- Fig. 2 Proposed sequence for the cracking of tetralin
- Fig. 3 Proposed sequence for the hydrogenation and cracking of 1-methylnaphthalene
- Fig. 4 Proposed sequence for the hydrogenation and cracking of 1-naphthol

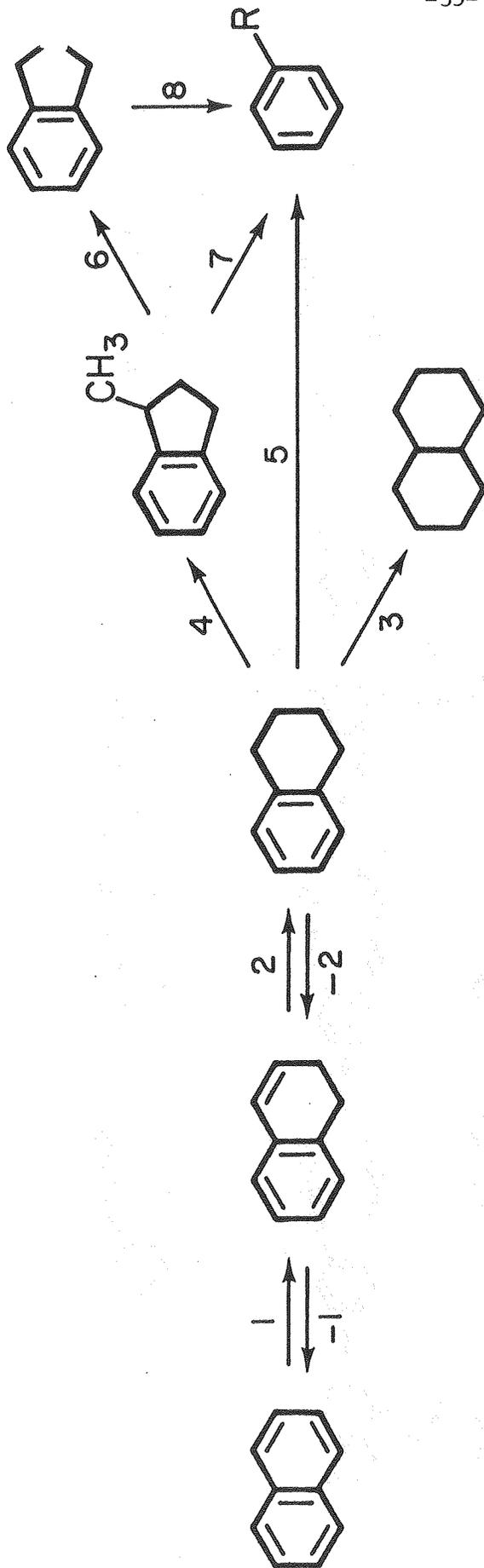


Figure 1.

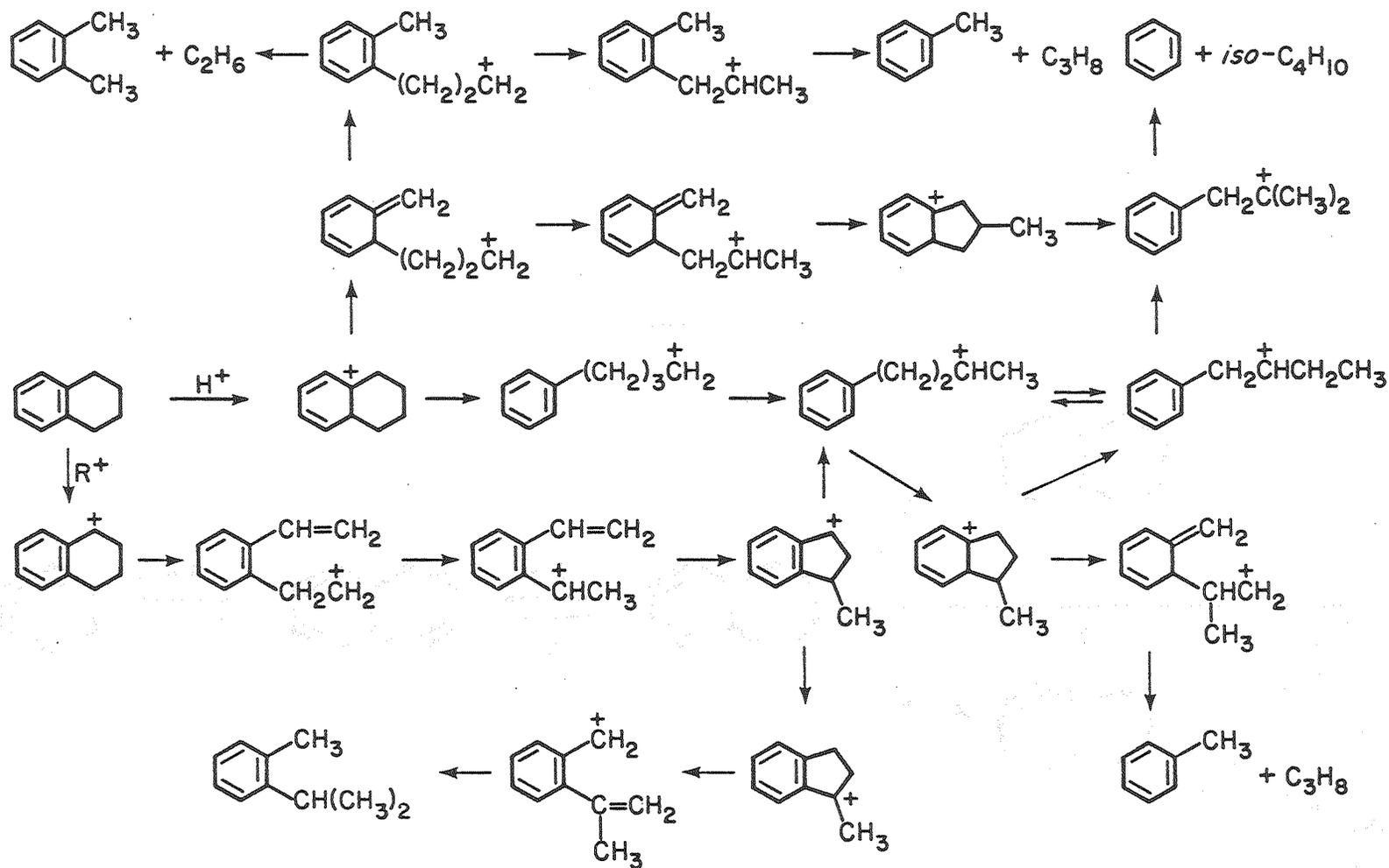


Figure 2.

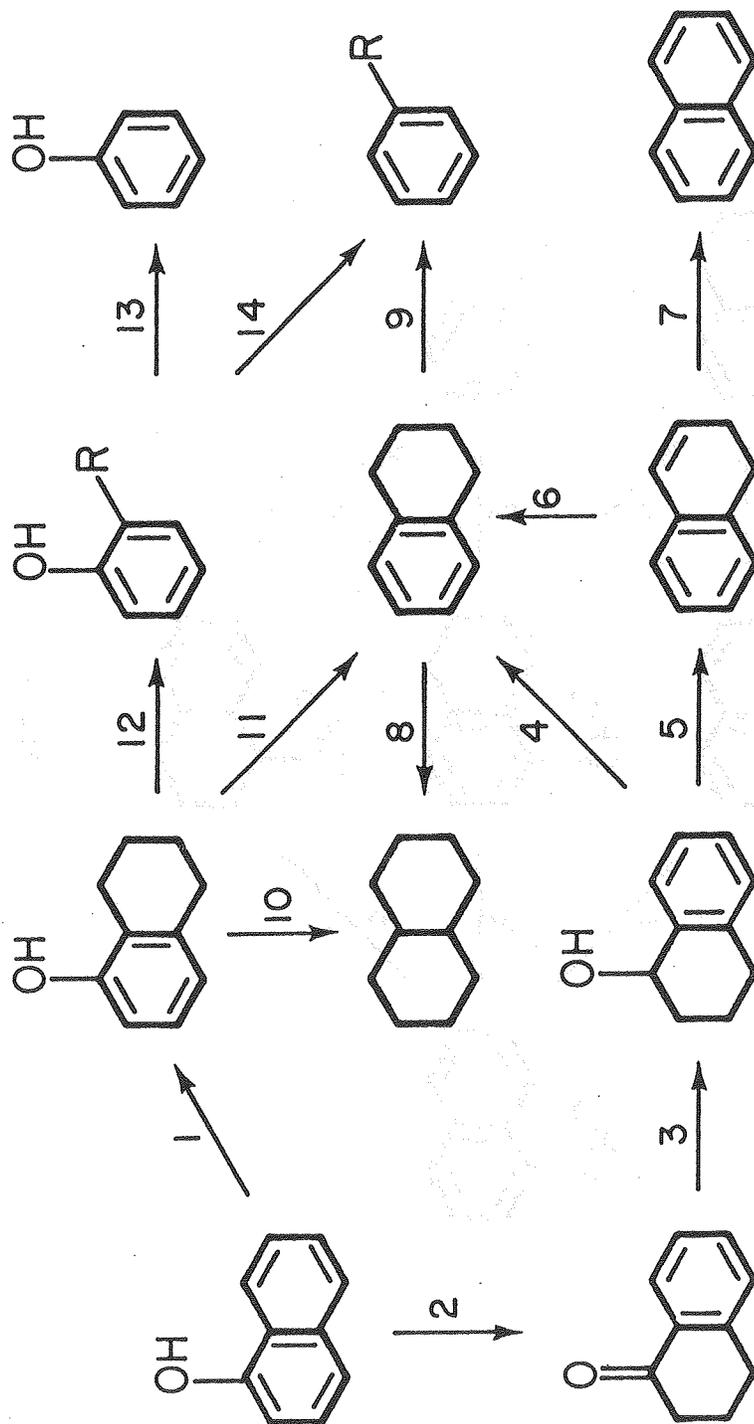


Figure 4.